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Persistence of Artificial Sweeteners
in a
15-Year-Old Septic System Plume

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Abstract

Groundwater contamination from constituents such as NO_3^- , often occurs where multiple sources are present making source identification difficult. This study examines a suite of major ions and trace organic constituents within a well defined septic system plume in southern Ontario, Canada (Long Point site) for their potential use as wastewater tracers. The septic system has been operating for 20 years servicing a large, seasonal-use campground and tritium/helium age dating indicates that the 200 m long monitored section of the plume is about 15 years old. Four parameters are elevated along the entire length of the plume as follows; the mean electrical conductivity value (EC) in the distal plume zone is $926 \mu\text{S}/\text{cm}$ which is 74% of the mean value below the tile bed, Na^+ ($14.7 \text{ mg}/\text{L}$) is 43%, an artificial sweetener, acesulfame ($12.1 \mu\text{g}/\text{L}$) is 23% and Cl^- ($71.5 \text{ mg}/\text{L}$) is 137%. EC and Cl^- appear to be affected by dispersive dilution with overlying background groundwater that has lower EC but has locally higher Cl^- as result of the use of a dust suppressant (CaCl_2) in the campground. Na, in addition to advective dilution, could be depleted by weak adsorption. Acesulfame, in addition to the above processes could be influenced by increasing consumer use in recent years. Nonetheless, both Na^+ and acesulfame remain elevated throughout the plume by factors of more than 100 and 1000 respectively compared to background levels, and are strong indicators of wastewater impact at this site. EC and Cl^- are less useful because their contrast with background values is much less (EC) or because other sources are present (Cl^-). Nutrients (NO_3^- , NH_4^+ , PO_4^{3-} , K^+) and pathogens (*E. coli*) do not persist in the distal plume zone and are less useful as wastewater indicators here. The artificial sweetener, acesulfame, has persisted at high concentrations in the Long Point plume for at least 15 years (and this

timing agrees with tritium/helium-3 dating) and this compound likely occurs at uniquely high concentrations in domestic wastewater. As such, it holds considerable promise as a powerful new tracer of wastewater impact in groundwater.

Introduction

Groundwater contamination from constituents such as nitrate often occurs where multiple sources are present making source identification difficult. Groundwater impacted by agricultural fertilizer and manure applications often has domestic wastewater disposal occurring in the same area and their compositions can be similar. Also in semi-arid regions such as the US southwest, infiltration basins that use reclaimed wastewater are widely used to augment aquifer recharge. Here there is a need to quantify the fraction of wastewater-sourced groundwater reaching adjacent production wells so that the extent of subsurface renovation can be established (Quast et al., 2006). Thus, there is an interest in identifying constituents that serve as intrinsic tracers of wastewater input. Nutrients and pathogens can be affected by a variety of subsurface immobilization and degradation reactions such as vadose zone immobilization (pathogens), denitrification (NO_3^-), anammox (NO_3^- and NH_4^+) and adsorption (PO_4^{3-} and K^+), making these parameters generally less useful as wastewater indicators. The minor constituent Boron (B) is mobile and persistent in groundwater and is usually elevated in domestic wastewater by a factor of about five (0.3-1 mg/L) compared to background groundwater, as a result of its use in laundry detergents. Wastewater B is also usually isotopically distinct from natural sources (Barth, 1998) and has been used successfully as an intrinsic wastewater tracer in both groundwater (Vengosh et al., 1994; Bassett et al., 1995; Bussey and Walter, 1996)

and surface waters (Chatelat and Gaillardet, 2005). However concentration contrasts with background values are relatively small, and wastewater B isotopic signatures can overlap with those of other sources, such as natural B occurring in saline groundwater (Bassett et al., 1995).

Some trace organic constituents that are relatively unique to domestic wastewater persist during sewage treatment and have been used successfully as wastewater tracers in both surface waters and groundwater. These include compounds such as carbamazepine and crotamiton found in pharmaceutical and personal care products (Clara et al., 2004; Heberer et al., 2004; Nakada et al., 2008; Sabourin et al., 2010), ibuprofen (Carrara et al., 2008), caffeine (Buerge et al., 2003) and estrogen active compounds (Quanrud et al., 2004). However, the degree to which these compounds persist in groundwater flow systems over multiyear and decadal timeframes has not yet been well established.

More recently, several artificial sweeteners widely used in the food and beverage industry have also been shown to resistant breakdown during sewage treatment and to persist quantitatively in surface water and groundwater environments (Buerge et al., 2009; Van Stempvoort et al., 2011a; Van Stempvoort et al., 2011b). These have also been suggested as potential wastewater tracers, however their longer term persistence in subsurface environments has not yet been established. In this study, our objective was to assess a spectrum of wastewater related parameters within a septic system plume that could be traced over a longer term, multiyear timeframe. The site selected was a large septic system servicing a seasonal use campground at Long Point, ON, Canada, where a well defined groundwater plume is present in an unconfined sand aquifer. Groundwater monitoring in the Tile Bed 2 area (Fig. 1) has been ongoing since it was commissioned in

92 1990 and the fate of a variety of constituents in the groundwater plume have been
 93 reported previously including; NO_3^- and NH_4^+ (Aravena and Robertson, 1998; Robertson
 94 et al., 2012), PO_4^{3-} (Robertson, 2008); pharmaceutical compounds (Carrara et al., 2008;
 95 Sabourin et al., 2010) and the artificial sweeteners, cyclamate, saccharin, sucralose and
 96 acesulfame (Van Stempvoort et al., 2011b). Several pharmaceutical compounds including
 97 carbamazepine and ibuprofen and several of the sweeteners, particularly acesulfame,
 98 which was approved for use in Canada in 1988 (Gougeon et al., 2004), persist in the
 99 plume, but the monitoring network used previously only extended 17-25 m from the tile
 100 bed and only intercepted the portion of the plume that was about one year old. However,
 101 because the septic system is 20 years old, a much longer plume is present at the site. For
 102 the current study the groundwater monitoring network was expanded in 2010, by the
 103 installation of an additional 23 multilevel, bundle piezometers extending up to 200 m
 104 downgradient from the tile bed. Then, on October 27, 2010, a detailed sampling sweep
 105 was initiated for a suite of parameters including EC, nutrients (NO_3^- , NH_4^+ , PO_4^{3-}), other
 106 major ions (Cl^- , SO_4^{2-} , Na^+ , K^+ , Ca^{2+}), pathogens (*E. coli*), the four artificial sweeteners
 107 and a suite of pharmaceutical compounds, from up to 90 groundwater monitoring points
 108 located along the plume centreline and upgradient from the tile bed. This was followed
 109 by trace gas sampling at seven monitoring points along the plume in January 2011, to
 110 allow tritium/helium ($^3\text{H}/^3\text{He}$) age dating of the plume. This manuscript reports on the
 111 persistence of the major ions and artificial sweeteners in the extended plume and provides
 112 a plume age profile. The distribution of the pharmaceutical compounds will be reported
 113 in a subsequent manuscript. Additionally, breakthrough behaviour of the major ions and

sweeteners at the water table below the tile bed, during the spring 2011 campground start up, is reported.

Long Point Site

The Long Point campground located on the north shore of Lake Erie (Fig. 1), has 256 overnight campsites and is open seasonally from mid-May until mid-October. Sewage from a single washroom facility is treated on-site, in a conventional septic system consisting of a septic tank and to two separate tile beds ($\sim 290 \text{ m}^2$ each) which are intermittently dosed using a float activated pump. Tile Bed 2, which is focus of the current study (Fig. 1), is located on sand where the water table is $\sim 2 \text{ m}$ deep. Loading to the tile beds was estimated previously at $\sim 10 \text{ cm/day}$ during peak loading in the summer (Robertson and Cherry, 1992), which is about 10 times higher than for smaller household septic systems. Water limiting fixtures installed in the washroom in ~ 2004 , result in relatively high concentrations of constituents such as nitrogen (100 mg/L , Table 1) in the wastewater, which is about twice as high as typically occurs in domestic septic tank effluent (e.g. $30\text{-}70 \text{ mg/L}$, Hinkle et al., 2008). The plume from Tile Bed 2 flows southward toward the Lake Erie shoreline (Fig. 1) within a $\sim 5 \text{ m}$ thick unconfined calcareous sand aquifer which is underlain by a less permeable clayey silt unit. Additional coring undertaken during this study revealed that the contact between the sand and silt units is sharp and is very flat lying throughout the study area (Fig. 2).

Groundwater ages in the proximal plume zone were estimated previously from seasonal breakthrough of EC peaks and from two NaBr tracer tests (Robertson et al., 2012) and vary from about seven days in the shallow water table zone below the tile bed

(during heavy sewage loading) to about one year, 17 m down gradient from the edge of the tile bed. There is also a strong vertical component of flow below the tile bed (up to ~10 cm/day, Robertson et al., 2012) as a result of the high sewage loading rate.

With the exception of the introduction of water limiting fixtures in the washroom in ~2004, which increased concentrations of Cl^- and NH_4^+ in the septic tank effluent by about 50-100% (Table 2), wastewater composition appears to have remained relatively stable over the 20 year operational period (Table 2). The site is thus well suited for examining longer term persistence of potential tracer constituents.

Methods

Monitoring Wells

In the current study, the existing monitoring network of 13 multilevel bundle piezometers (wells 100-140, Fig. 1) was expanded by the installation of an additional 23 multilevel bundles in the down gradient area (wells 1-23, Fig. 1). These each consist of from 6-13 variable depth sampling points of 3-6 mm dia. polyethylene tubing with short, 5 cm long, slotted and screened tips. Each bundle was installed using direct-push casing, into a single borehole, without the use of filter sand or sealing material. Twenty two of the bundles, with a total of 90 monitoring points, are aligned along section A-A', which follows the centreline of the plume. These include two upgradient bundles (127, 140, Fig. 1) which are located within a naturally grassed savannah area that is minimally impacted by anthropogenic activity. Downgradient of the tile bed, the plume migrates under the campground area and precipitation recharge occurring in this area could be affected by a

variety of anthropogenic influences such as food and beverage spillage at the campsites and the annual application of a dust suppressant (CaCl_2) to the roadways shown on Fig. 1.

Plume Sampling and Analyses

Site characterization methods including sediment coring, piezometer installation and groundwater sampling have been described previously (Robertson and Cherry, 1992; Aravena and Robertson, 1998; Robertson, 2008). Most of the data in the current study is from a sampling sweep initiated on October 27, 2010. Much of the sampling was completed on October 27, although infill and repeat sampling continued for up to 30 days thereafter. Additionally, during April-July 2011, time series sampling ($n = 12$) was undertaken in the shallow water table zone below the tile bed (well 122-2.2 m depth) and from the septic tank effluent ($n = 10$), to observe seasonal breakthrough trends of potential tracer constituents at the water table immediately after the campground was opened for the season on May 15, 2011. Groundwater samples were collected using a peristaltic pump with silicone tubing and were filtered ($0.45 \mu\text{m}$) in-line, prior to atmospheric exposure. Samples for cation, NH_4^+ and PO_4^{3-} analyses were acidified to $\text{pH} < 2$ immediately after collection, whereas samples for anions, NO_3^- and artificial sweeteners were left untreated. All samples were immediately transported to the laboratory where they were either refrigerated at $\sim 4^\circ \text{C}$ or frozen (sweetener and NH_4 samples) until analysis. Nitrate, Cl^- and SO_4^{2-} were analyzed in the Environmental Geochemistry Laboratory (EGL), Department of Earth and Environmental Sciences, University of Waterloo, ON, by ion chromatography using a Dionex ICS-90 (Dionex, Sunnyvale, CA), which provided an analytical reporting limit of $< 0.5 \text{ mg L}^{-1}$ for each of these parameters.

182 NH_4^+ was also analyzed at EGL, using a colourimetric technique with a Beckman DU
 183 530 spectrophotometer, which provided a detection limit of $<0.05 \text{ mg L}^{-1} \text{ N}$. PO_4^{3-} was
 184 analyzed at the Soil and Nutrient Laboratory, University of Guelph, ON using a
 185 colorimetric technique (cadmium reduction) with a Technicon TRAACS-800
 186 autoanalyzer (Technicon Instruments, Tarrytown, NY), which provided a detection limit
 187 of $0.05 \text{ mg L}^{-1} \text{ P}$. Cations were analyzed at Canada Centre for Inland Waters (CCIW),
 188 Burlington, ON, using an Inductively Coupled Plasma technique that provided detection
 189 limits of $0.005\text{-}0.01 \text{ mg/L}$. The four artificial sweeteners were also analyzed at CCIW,
 190 by ion chromatography (Dionex 2500 system) coupled with tandem mass spectrometry
 191 (AB Sciex QTRAP 5500 triple-quadrupole), following the methods described by Van
 192 Stempvoort et al. (2011a). This technique provided a detection limit of $5 \text{ }\mu\text{g/L}$ for
 193 sucralose and much lower detection limits for sacharrin ($0.021 \text{ }\mu\text{g/L}$), cyclamate (0.003
 194 $\mu\text{g/L}$) and acesulfame ($0.008 \text{ }\mu\text{g/L}$).

$^3\text{H}/^3\text{He}$ dating

196
 197 Seven new 5 cm diameter wells were also installed along the plume centreline in
 198 2010, to facilitate trace gas sampling for $^3\text{H}/^3\text{He}$ age dating of the groundwater (Solomon
 199 and Cook, 2000). These wells had short, 30 cm long, screened tips installed into the
 200 plume core zone at locations immediately adjacent to wells 4 (4.4 and 6.4 m depth), well
 201 7 (6.5 m), well 23 (6.5 m), well 14 (7.5 m), well 20 (6.5 m) and well 22 (6.4 m).
 202 Sampling occurred by inserting diffusion-type samplers (Gardner and Solomon, 2009)
 203 consisting of two 5 cm lengths of 4 mm dia. copper tubing connected with a 5 cm length
 204 of 4 mm diameter, gas permeable silicone tubing. After purging the wells, the samplers



were inserted to the screen depths, for a period of one week during January 2011. Upon removal from the wells, the copper tubes were immediately crimped and then shipped to the Dissolved Gas Laboratory, University of Utah, Salt Lake City, UT, for analysis. Noble gas analyses occurred by cryogenic separation followed by the measurement of ^3He and ^4He on a MAP215-50 sector field mass spectrometer, and Ne, Ar, Kr, and Xe measured on a quadrupole mass spectrometer operated in static mode. Coincident with trace gas sampling, a 1L sample was retrieved from each well for analysis of tritium (^3H) content. These were analyzed at the Environmental Isotope Laboratory, University of Waterloo, after enrichment, which provided a reporting precision of $\pm 0.8\text{-}0.9$ TU. Then in February 2011, total dissolved gas pressures were measured in the seven trace gas wells by inserting a downhole pressure probe (PT4 Tracker, Point Four Systems Inc., Coquitlam, BC, Canada) to the well screen depth and then slowing pumping the wells at a rate that caused minimal drawdown (~ 0.5 L/min) until stable readings were obtained, generally after about one hour. This is the procedure recommended by Roy and Ryan (2010) to avoid measuring stagnant well bore water that may be partially degassed.

Results and Discussion

Plume Ages

As shown in Tables 3 and 4, dissolved Ne concentrations are all less than the atmospheric equilibrium value, indicating that gas stripping has occurred. The ΔNe values listed in Table 4 represent the percent deviation from atmospheric equilibrium and range from -32% to -88%. The loss of noble gases appears to result from denitrification that also produces total dissolved gas pressures that are significantly greater than the



228 atmospheric value (939 to 1046 mmHg for TDGP versus 756 for barometric pressure,
229 table 4). At shallow depths near the tile bed, the TDGP is only slightly less than the
230 confining pressure head (barometric pressure plus hydrostatic pressure), but this
231 difference increases at greater depths and greater distances from the tile drains (Table 4).
232 When the total dissolved gas pressure approaches or exceeds the confining pressure,
233 bubbles may form and result in stripping of sparingly soluble gases such as Ne and He
234 from the water. While it is clear from Table 4 that gas stripping is not occurring along
235 the axis of the plume (i.e. total dissolved gas pressures are always less than the confining
236 pressure), it is also apparent that at shallower depths near the water table beneath the tile
237 bed, gas stripping is likely. Furthermore, on a number of occasions it was observed that
238 some piezometer tubes (0.6 cm dia.) located near the tile bed would spontaneously erupt
239 without pumping. During these events an intermittent column of water and gas would
240 eject from the tubing for a period of about half a minute, thus degassing was actually
241 observed near the tile bed. These eruptions occurred only near the tile bed where
242 denitrification activity was most intense, and were not observed farther downgradient.
243 We have used these TDGP observations to formulate a model for calculating $^3\text{H}/^3\text{He}$ ages
244 that takes into account gas loss due to stripping. We followed the approach of Visser et
245 al. (2007), but included the occurrence of terrigenous ^4He , and we considered two end-
246 member cases of the stripping occurring either at the water table, or at the well (e.g.
247 stripping during sample collection). When stripping occurs near the water table
248 atmospheric He and Ne (that are used to separate tritiogenic from atmospheric ^3He
249 (Solomon and Cook, 2000)) are affected, but not the absolute amount of tritiogenic ^3He .
250 When stripping occurs at sampling, both atmospheric and tritiogenic ^3He are affected.



The general case where stripping occurs at some arbitrary point along a flow path requires additional information or assumptions about where the stripping occurs (Visser et al., 2007). Equations for calculating the apparent $^3\text{H}/^3\text{He}$ age under the conditions of stripping at the water table and at the time of sampling are derived in Appendix A (Supplemental Material). In addition to the loss of atmospheric gases, it is clear from Table 4 that ^4He is being produced in the subsurface as it increases systematically with distance along the plume. The age equations shown in Appendix A include a subsurface source of ^4He known as terrigenic helium (Solomon and Cook, 2000) that results from the decay of U and Th in the aquifer. While it is ^3He that is used for $^3\text{H}/^3\text{He}$ dating, the production of ^4He should be accompanied by a small production of ^3He and this is taken into account by specifying the ratio of $^3\text{He}/^4\text{He}$ of this source, known as $R_{\text{terrigenic}}$.

Figure 3 shows $^3\text{H}/^3\text{He}$ ages in the plume core zone computed assuming that stripping occurs at the water table. Apparent age values are shown for two end-member cases for $R_{\text{terrigenic}}$ of 2×10^{-8} and 4×10^{-7} . While an independent evaluation of $R_{\text{terrigenic}}$ is not available for this site, a value of 4×10^{-7} results in an age distribution that is approximately 0 at the water table beneath the tile bed, and is more consistent with other site data as explained below. In any case, the apparent ages range from 2 to 5 years in well 24, 4.4 and 6.0 m depths, located 20 m from the edge of the tile bed, then increase systematically along the plume to a maximum age of 13 to 17 years in well 22, 6.5 m depth, located 200 m from the tile bed. The well 24 ages are corroborated by a previous NaBr tracer test conducted in 2008 (Robertson et al., 2012), which showed that the plume at well 124, 3 m depth, which is slightly closer (17 m from the edge of the tile bed), had a slightly younger age of 0.8 years. The age indicated overall horizontal groundwater



velocity of the plume ($200 \text{ m}/15 \text{ yrs} = 13 \text{ m/yr}$) is slightly slower, but is in general agreement with, previous estimates of horizontal velocity in the shallower plume zone closer to the tile bed (23 m/yr), based on seasonal breakthrough of an elevated EC spike (Robertson, 2008). The approximate 15 year age estimate at the most distal location (well 22) implies that the current monitoring network has sampled about three quarters of the total plume length. Both the systematic increase in the $^3\text{H}/^3\text{He}$ ages and the TDGP being less than the confining pressure, support a model of degassing occurring near the water table. Alternatively, if it is assumed that degassing occurred in the well at the time of sampling, unrealistically old ages of 30-40 years are obtained at several locations mid-distance along the plume.

Distribution of Indicator Parameters

Figure 2 shows the distribution along the centreline, of three parameters (Cl^- , Na^+ and EC) that are often elevated in contaminant plumes and that have been used previously as indicator parameters. Figure 4 profiles the concentrations of these constituents along the plume core zone and in the upgradient wells, and compares these to mean values measured in the septic tank effluent (Table 1). EC remains elevated throughout the plume core zone ($903\text{-}1616 \mu\text{S/cm}$) which contrasts with lower values in the up-gradient wells ($379\text{-}500 \mu\text{S/cm}$) by a factor of 2-4. Cl^- is more distinctly elevated in the plume ($31\text{-}99 \text{ mg/L}$), which is 3-150 times higher than in the upgradient wells ($0.6\text{-}13 \text{ mg/L}$). However in the down gradient area, some of the groundwater overlying the plume has very high Cl^- of up to 112 mg/L , which is higher than in the plume. This is likely a result of the use of the dust suppressant CaCl_2 on the campground roadways. Na^+ ,



on the other hand is consistently elevated throughout the plume (11-49 mg/L) at concentrations that are generally >100 times higher than values occurring in both in the upgradient wells and in the CaCl₂ impacted wells.

Distribution of Nutrients and Pathogens

Figure 5 shows the distribution of three nutrients that are normally elevated in domestic wastewater (NH₄⁺-N, NO₃⁻-N and PO₄³⁻-P) and E. coli. bacteria, along the plume centreline. Figure 6 profiles the concentrations of the nutrients along the core zone. The nutrients are elevated in the septic tank effluent (8-100 mg/L, Table 1) and occur intermittently at similarly high concentrations in the shallow groundwater below the tile bed (NH₄⁺-N up to 20 mg/L; NO₃⁻-N up to 103 mg/L and PO₄³⁻-P up to 6.8 mg/L). However, beyond 50 m from the tile bed, all of these constituents decline to non-detectable levels, indicating that significant attenuation has occurred. This is consistent with previous studies at this site which showed that; NO₃⁻ is depleted by denitrification, utilizing trace quantities of organic carbon and pyrite present in the aquifer sediments (Aravena and Robertson, 1998), that NO₃⁻ and NH₄⁺ are also attenuated by anaerobic ammonium oxidation (anammox, Robertson et al., 2012) and that PO₄³⁻ migration velocity is retarded by a factor of about 25 by adsorption (Robertson, 2008). These constituents are thus less useful as indicator parameters at this site because of these vigorous attenuation processes. The low level NH₄⁺-N that occurs in the distal plume zone (1-3 mg/L, Fig. 5) has an isotopic signature that is distinctly lighter (¹⁵N = +4.3 ± 1.2 per mil, n=5, EGL internal data) compared to the wastewater NH₄⁺-N that occurs immediately downgradient of the tile bed (¹⁵N = +19 ± 6.4 per mil, n= 25, Robertson et

al., 2012) and is therefore not likely of wastewater origin. This could represent natural NH_4^+ mineralized from organic rich zones that may be present near the base of the aquifer or in the underlying silt unit.

Distribution of other Major Ions

Figure 7 shows the distribution of several other major ions (K^+ , Ca^{2+} , SO_4^{2-} -S) along the plume centreline, while Fig. 4 profiles the concentrations of K^+ and Ca^{2+} along the core zone. K^+ is elevated in the proximal plume zone (6-47 mg/L) by a variable factor of about 1-400 compared to the upgradient wells, however in the distal plume zone K^+ concentrations (2-5 mg/L) are virtually the same as in the overlying background groundwater. Elevated K^+ values in the proximal plume (>5 mg/L) decline abruptly beyond 115 m from the tile bed, which may be suggestive of a sorption front with indicated retardation factor of about 2-3. This is consistent with K^+ retardation factors observed in other contaminant plumes in sand aquifers (2-4, Nicholson et al., 1983; Ceazan et al., 1989). Ca^{2+} in the plume (120-269 mg/L) is elevated by a factor of 2-4 compared to both the upgradient wells and the septic tank effluent. Presumably this is a result of calcite dissolution that occurs in response to acidity generated by the wastewater oxidation reactions occurring in the vadose zone, particularly NH_4^+ oxidation. SO_4^{2-} -S is sporadically elevated in the plume, with highest values (up to 50 mg/L) occurring in the basal zone where NO_3^- becomes depleted. Presumably this reflects denitrification utilizing pyrite from the aquifer sediments as the electron donor (Aravena and Robertson, 1998).

Distribution of Artificial Sweeteners

Figure 8 shows the distribution of the four artificial sweeteners (acesulfame, cyclamate, sucralose, saccharin) along the plume centreline, while Fig. 9 profiles the concentrations of these constituents along the plume core zone. All four sweeteners occur in the septic tank effluent at similar mean concentrations (15-51 $\mu\text{g/L}$, Table 1). However, whereas acesulfame and sucralose persist in the proximal plume at concentrations that are similar to the septic tank effluent, cyclamate and sacharrin occur at much lower concentrations in the plume ($<10\%$ of tank values), indicating that they are likely influenced by degradation reactions in the vadose zone. Although sucralose is elevated throughout the proximal plume zone (15-77 $\mu\text{g/L}$), it has a much higher analytical detection limit (5 $\mu\text{g/L}$) compared to the other compounds (0.003-0.02 $\mu\text{g/L}$) and is thus only elevated by a factor of 3-15 compared to background values. Also sucralose values decline abruptly to background levels beyond 60 m from the tile bed. This could reflect a sorption front or it could indicate increasing consumer use of this sweetener in recent years. Acesulfame on the other hand, because of its much lower detection limit, is elevated by a much larger factor (>1000) compared to background values even in the distal plume zone 200 m from the tile bed (8-18 $\mu\text{g/L}$). There is no evidence of abrupt acesulfame depletion anywhere along the plume. Although cyclamate is considerably attenuated in the plume compared to the effluent, it does persist throughout the distal plume zone at concentrations of 1-2 $\mu\text{g/L}$, which still represents enrichment by a factor of ~ 500 compared to background detection limit values.

Persistence of EC, Cl, Na, and Acesulfame

366 Figure 10 shows normalized concentration profiles (C/C_o) of four constituents
 367 (EC, Cl^- , Na^+ and acesulfame) that appear relatively mobile and persistent along the full
 368 length of the plume. Comparing normalized values could provide insight into processes
 369 that may be affecting these constituents differently. Initial concentrations (C_o) were
 370 calculated as the mean values measured in the four multilevel bundles underlying the tile
 371 bed (wells 120-123), because these provide a larger data set ($n = 20$) that probably better
 372 reflects effluent composition and loading under all seasonal conditions. With the
 373 exception of Cl^- , which begins to increase beyond 150 m from the tile bed, all of these
 374 parameters show similar slow declining trends along the plume without abrupt changes.
 375 In the distal plume zone (wells 21 and 22), the mean EC value ($926 \mu S/cm$, $n = 4$) is 74%
 376 of the mean value below the tile bed, Na^+ (14.7 mg/L) is 43%, acesulfame ($12.1 \mu g/L$) is
 377 23% and Cl^- (71.5 mg/L) is 137%. EC and Cl^- appear to be affected by dispersive
 378 dilution with overlying background groundwater that has lower EC but which has locally
 379 higher Cl^- as result of the use of $CaCl_2$ on the campground roadways. Na, in addition to
 380 advective dilution, could be depleted by weak adsorption. Acesulfame, in addition to the
 381 above processes could be influenced by increasing consumer use in recent years,
 382 although we are not aware of any records that document usage trends in Canada. Also,
 383 the introduction of water limiting fixtures in the washroom in ~2004, which has increased
 384 the effluent strength in recent years (Table 2), also likely contributes to the higher values
 385 observed near the tile bed. Nonetheless, all of these parameters (with the possible
 386 exception of Cl^-), remain indicative of the wastewater source throughout the full length of
 387 the plume. Furthermore, during campground start up in May 2011, all of these parameters
 388 (Cl^- , Na^+ and acesulfame), arrived at the water table below the tile bed simultaneously



(Fig. 11), indicating that none of these are strongly affected by sorption in the vadose zone sediments. Saccharin and cyclamate also arrived at the water table at the same time (Fig. 11), indicating a similar lack of sorption effect. However, the water table values for saccharin and cyclamate then both slowly declined to $< 1 \mu\text{g/L}$ by July 2011. The septic tank values for acesulfame ($43 \pm 8 \mu\text{g/L}$, $n=8$, May 24-July 8, 2011), saccharin ($12.4 \pm 2.9 \mu\text{g/L}$, $n = 8$) and cyclamate (36.5 ± 38.7 , $n = 8$) all remained consistently high throughout this period ($> 8 \mu\text{g/L}$). This behaviour indicates that both saccharin and cyclamate are affected by degradation in the vadose zone (aerobic), although a seasonal acclimation period of several weeks duration is apparently required. Sucralose was not detected ($<5 \mu\text{g/L}$) in the septic tank effluent during the period May 24-June 15 ($n = 5$), for reasons that were not apparent, but then concentrations increased thereafter. Sucralose values at the water table (Fig. 11) closely mirrored septic tank values throughout this period.

Comparison of the normalized plots of EC , Na^+ , Cl^- and acesulfame along the plume (Fig. 10) suggests that over time, input concentrations of acesulfame in the wastewater may have increased at Long Point. Assuming that attenuation of acesulfame in the plume has been similar to that of the other indicators, particularly Na (i.e., negligible biodegradation), then on the basis of the observed trends in normalized concentrations at the various points along the plume, with inferred ages ranging from about 2-15 years, it appears that acesulfame concentrations may have increased steadily over the past 15 years, and that they may have doubled since ~1995 (the approximate age of the oldest part of the plume that was investigated). Given that there are no studies that have documented changes in acesulfame concentrations in ‘domestic’ wastewater in

Canada since its approval for use in 1988, this plume data is apparently the best available proxy / surrogate record of inferred changes in acesulfame concentrations in domestic wastewater in Canada. Even if the acesulfame trend is partly the result of slow biodegradation, the degradation rate must be exceedingly slow (half life > 15 years) and the acesulfame concentrations in the 1995 wastewater must have been at least 50% of current values.

Implications

Na^+ is monovalent cation that is affected by adsorption, but only weakly so, and in most aquifers its migration velocity is close to that of Cl^- (Nicholson et al., 1983; Dance and Reardon, 1983; Robertson et al., 1991). The simultaneous breakthrough of elevated Cl^- and Na^+ at the water table during spring 2011 startup, (Fig. 11), is consistent with a minimal sorption effect. Thus, Na^+ can be considered a mobile tracer in many aquifer environments. Furthermore, the Na^+ contrast with background groundwater at this site remains large (> 100), even in the downgradient area where there could be some anthropogenic influence from the campground. Na^+ was used previously as the preferred intrinsic tracer for identifying a septic system plume in agricultural terrain in southern Ontario (Cambridge site, Robertson et al., 1991) because Na^+ remained low in the background groundwater (mean of 4 mg/L) compared to much higher values in the septic system plume (mean of 86 mg/L). However, in a larger scale (12 km²) regional survey of shallow (<30 m) overburden wells (n = 29), in other agricultural terrain near the city of Woodstock, also in southern Ontario, considerably higher Na^+ values, mostly in the range of 5-25 mg/L, were observed (Heagle, 2000). Higher Na^+ values in the Woodstock area,

likely reflected additional input from road salt and manure applications, making Na^+ less useful as a wastewater tracer in such areas.

The persistence of acesulfame throughout the plume at concentrations more than 1000 times higher than background detection-limit values, points to the considerable potential of this trace organic constituent as an intrinsic wastewater tracer. Such high enrichment offers the potential to allow detection of even very small inputs from wastewater. Acesulfame was also detected previously in 65 of 100 monitoring wells sampled near Zurich Switzerland (Buerge et al., 2009) and in more than 60% of ~300 samples collected in a broad-based screening survey in Canada (Van Stempvoort et al., 2011a), which included samples from groundwater wells in Ontario and the Yukon, groundwater along streams in Alberta, and surface water from five streams effected by urban development in Ontario and Alberta. Acesulfame concentrations should be further screened in other septic system plumes and in other groundwater environments. These should include agriculturally impacted sites because sweeteners can be included in animal feed formulations in some jurisdictions (Buerge et al., 2011) and could thus be present where groundwater is impacted by manure applications. If, however, acesulfame is shown to be uniquely enriched in domestic wastewater and remains mobile and persistent in other aquifer environments, then in cases of groundwater NO_3^- contamination for example, the ratio of NO_3^- /acesulfame might be developed as a new tool for establishing the faction of NO_3^- loading originating from agricultural versus domestic wastewater sources.

458

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- 557
- 558



559 Table 1. Mean composition of the Long Point septic tank effluent in recent studies (2007-
560 2011).

561

	Mean \pm s.d.	n
Major ions ⁽¹⁾ (mg/L)		
Cl ⁻ ^(1,2)	83 \pm 31	20
Na ⁺	36 \pm 9	10
Ca ²⁺	137 \pm 31	9
SO ₄ ²⁻ -S	6.6	1
K ⁺	25 \pm 8	10
Nutrients (mg/L)		
NH ₄ ⁺ -N ^(1,2)	100 \pm 27	23
NO ₃ ⁻ -N ⁽²⁾	<2	11
Sweeteners ^(1,3) (μg/L)		
Acesulfame	50 \pm 15	13
Sucralose	51 \pm 42	13
Cyclamate	29 \pm 37	13
Saccharin	15 \pm 5	13

562

563 1) May 19-July 8, 2011, this study

564 2) Sept 18, 2007-June 8, 2010, Robertson et al. (2012)

565 3) June, 2008- Oct 4, 2010, Van Stempvoort et al. (2011b)

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570

571 Table 2. History of wastewater composition in the Long Point septic tank effluent over
572 20 years of operation. Shown are mean values over 1-3 year periods (n, number of
573 samples).

574

Year	n	EC ($\mu\text{S}/\text{cm}$)	Cl^- (mg/L)	Na^+ (mg/L)	NH_4^+-N (mg/L)	$\text{PO}_4^{3-}-\text{P}$ (mg/L)	reference
1989-1990	6		44	35	66	6	Robertson and Cherry (1992)
1995	1		42	23	57	11.8	Robertson et al.(1998)
2004	2	1243	74	47	88	7.5	Carrara (2006); Robertson (2008)
2007-2010	10-13		67		106		Robertson et al. (2012)
2011	9-10	1662	97	36	92		This study

575

576



577

578 Table 3. Noble gas and tritium concentrations.

579

Well	Distance from source (m)	Ar (ccSTP/g)	Ne (ccSTP/g)	Kr (ccSTP/g)	Xe (ccSTP /g)	He (ccSTP/g)	R/Ra	Tritium (TU)
LP24-4.4	20	3.09E-04	1.29E-07	7.61E-08	1.03E-08	3.45E-08	0.874	10.0
LP24-6.0	23	2.53E-04	1.12E-07	6.59E-08	9.89E-09	3.69E-08	0.741	9.9
LP7-6.4	60	2.86E-04	1.34E-07	8.03E-08	1.13E-08	3.93E-08	0.896	10.7
LP13-6.5	95	1.37E-04	2.57E-08	4.22E-08	7.05E-09	4.33E-08	0.543	10.0
LP23-6.4	108	1.46E-04	3.72E-08	4.29E-08	7.44E-09	5.11E-08	0.502	9.2
LP20-7.3	160	1.77E-04	4.80E-08	5.09E-08	8.18E-09	4.73E-08	0.734	9.7
LP22-6.3	200	2.74E-04	1.13E-07	7.50E-08	1.12E-08	5.39E-08	0.878	9.1

580

581

582

583 Table 4. ΔNe , apparent ages with end-members values for R_{terr} , terrigenic ^4He , and
584 TDGP. Confining pressure (CP) is hydrostatic pressure at the well screen depth plus
585 atmospheric pressure of 756 mmHg.

586

Well	delta Ne %	Apparent Age (yr) with R_{terr} = $2\text{e-}8$	Apparent Age (yr) with R_{terr} = $4\text{e-}7$	Age error (yr)	$^4\text{He}_{\text{terr}}$ (ccSTP/g)	TDGP (mmHg)	CP (mmHg)
LP24-4.4	-33.5	4.8	2.7	0.4	9.4E-09	939	952
LP24-6.0	-41.7	5.4	1.9	0.4	1.6E-08	1029	1063
LP7-6.4	-32.2	6.7	4.3	0.4	1.2E-08	1032	1103
LP13-6.5	-88.4	12.7	6.5	0.5	3.9E-08	1046	1088
LP23-6.4	-82.6	13.5	5.8	0.5	4.5E-08	999	1040
LP20-7.3	-77.3	16.3	11.2	0.5	3.9E-08	988	1020
LP22-6.3	-43.7	16.9	12.7	0.6	3.2E-08	950	1016

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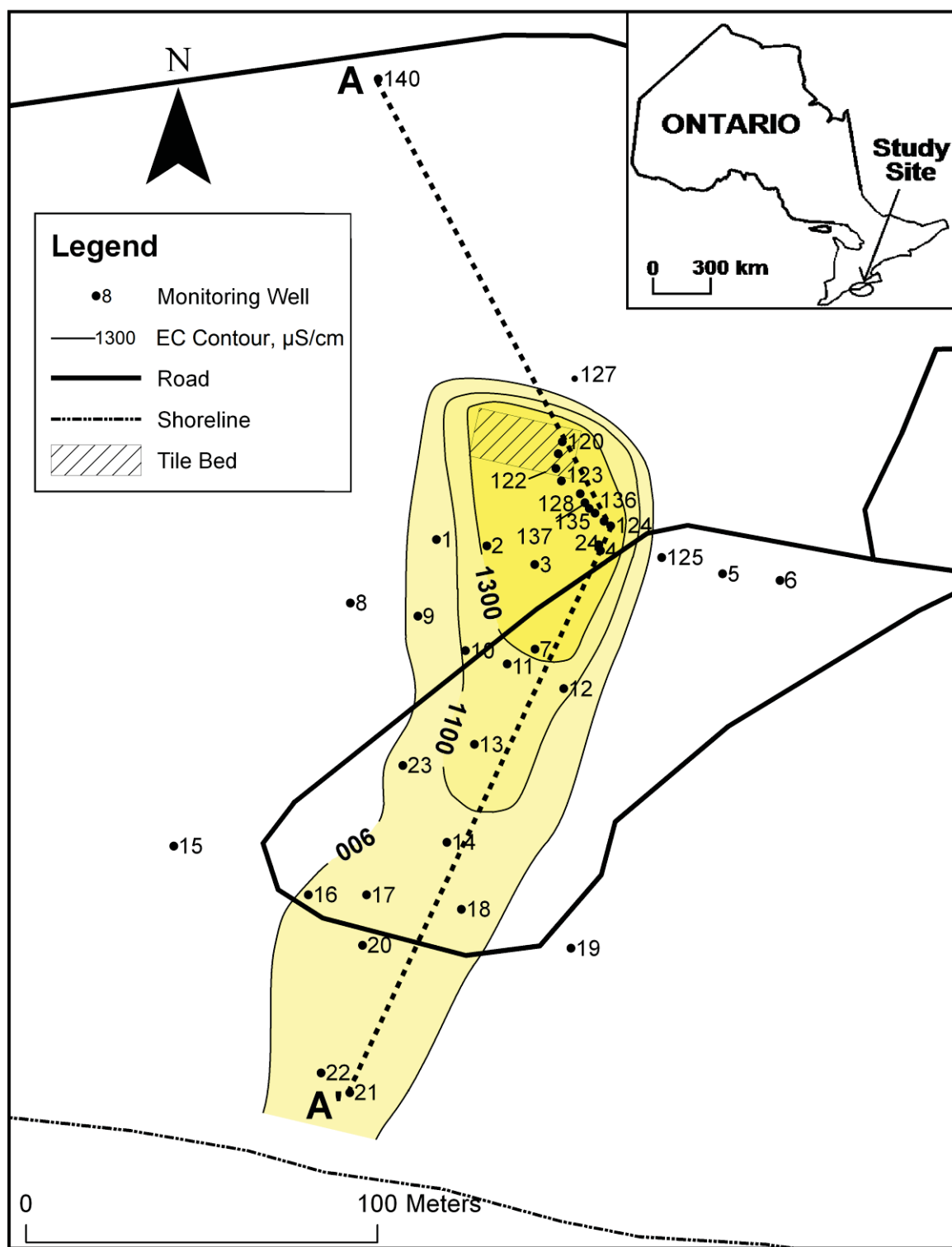


Fig. 1. Long Point septic system site showing location of the tile bed, multilevel monitoring wells and contours of maximum electrical conductivity (EC) measured in the monitoring wells October, 2010.

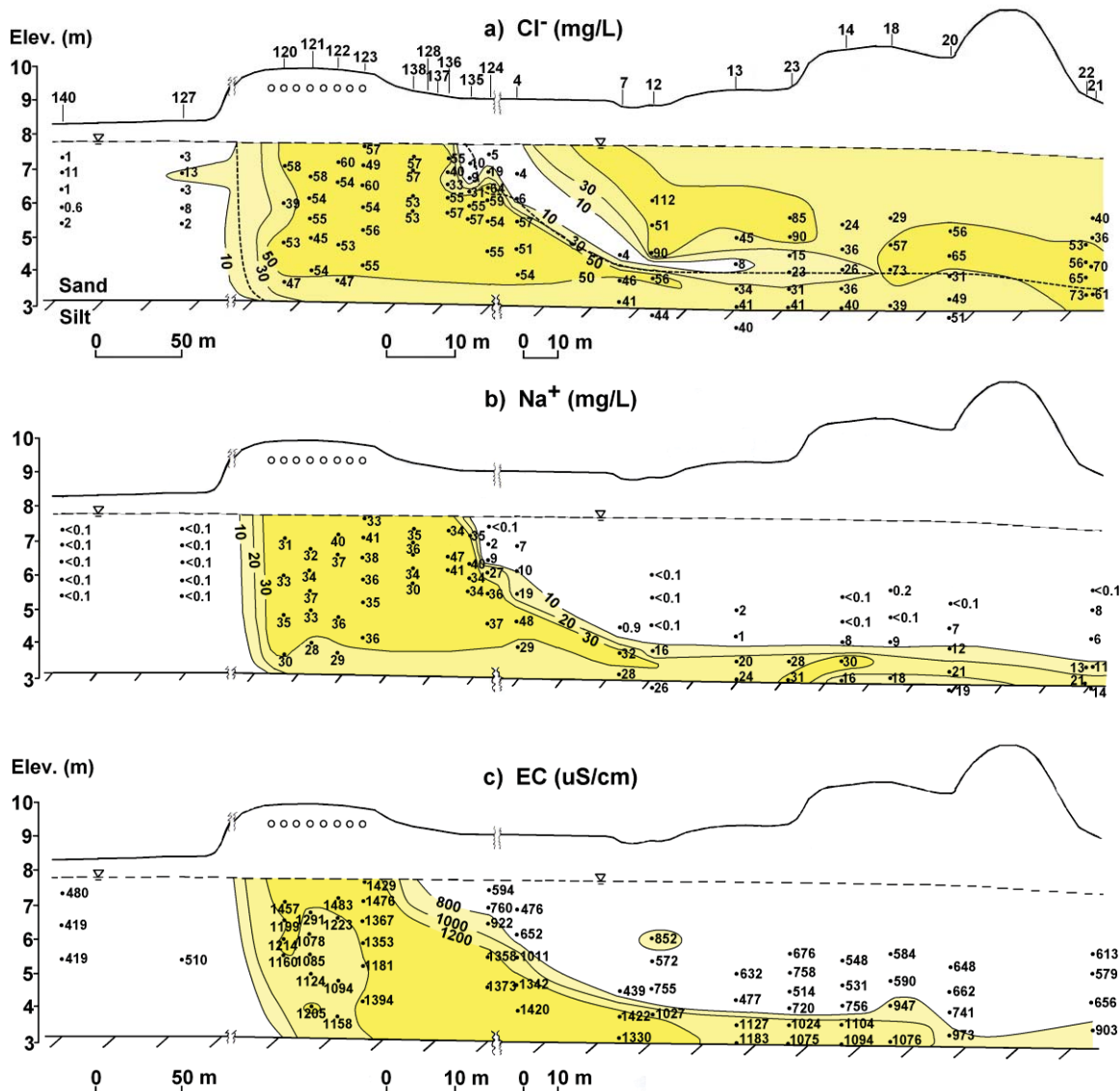


Fig. 2. Distribution of indicator parameters along the plume centreline, October, 2010: a) Cl^- , b) Na^+ and c) electrical conductivity (EC). Dashed line indicates plume core zone indicated by $\text{Na}^+ > 10$ mg/L. Note changes in distance scale.

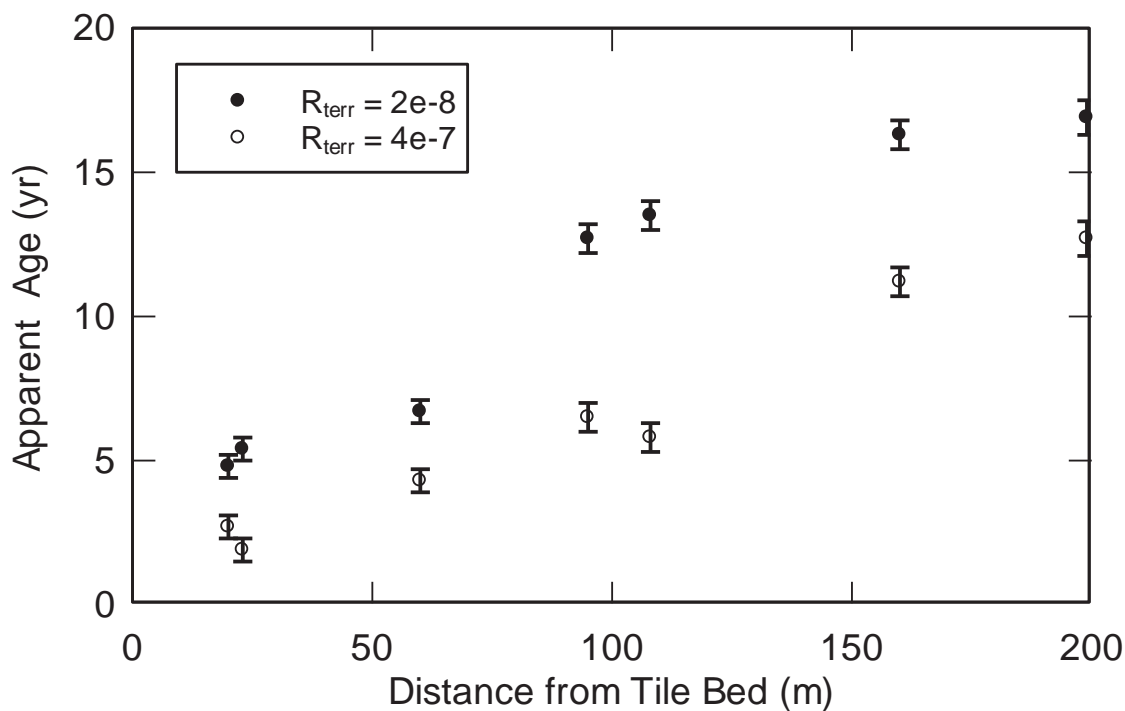
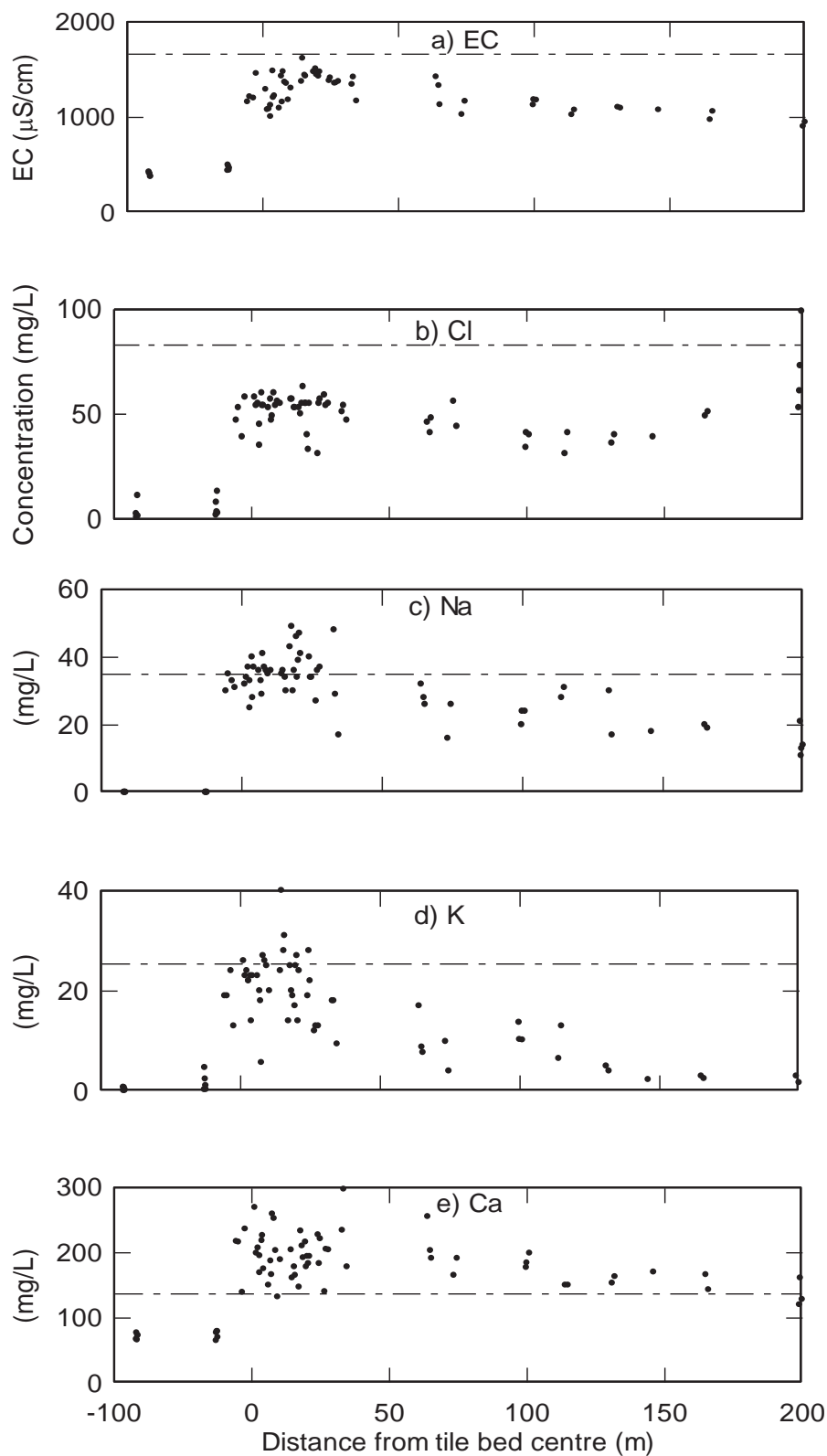


Fig. 3. Groundwater age profiles along the plume core zone determined by $^3\text{H}/^3\text{He}$ dating. Ages assume degassing occurred near the tile bed area. Ages were computed using two end-member values for ratio of $^3\text{H}/^4\text{He}$ for terrigenous He production (R_{terr}). The ages computed using $R_{terr} = 4 \times 10^{-7}$ are more consistent with the site data (see text).





619 Fig. 4. Concentration profiles of major ions along the plume core and in upgradient
620 wells: a) electrical conductivity (EC), b) Cl^- , c) Na^+ , d) K^+ and e) Ca^{2+} . Dashed line is
621 mean septic tank value from Table 1. Core zone wells defined by $\text{Na}^+ > 10 \text{ mg/L}$. Note
622 change of distance scale upgradient of the tile bed.
623

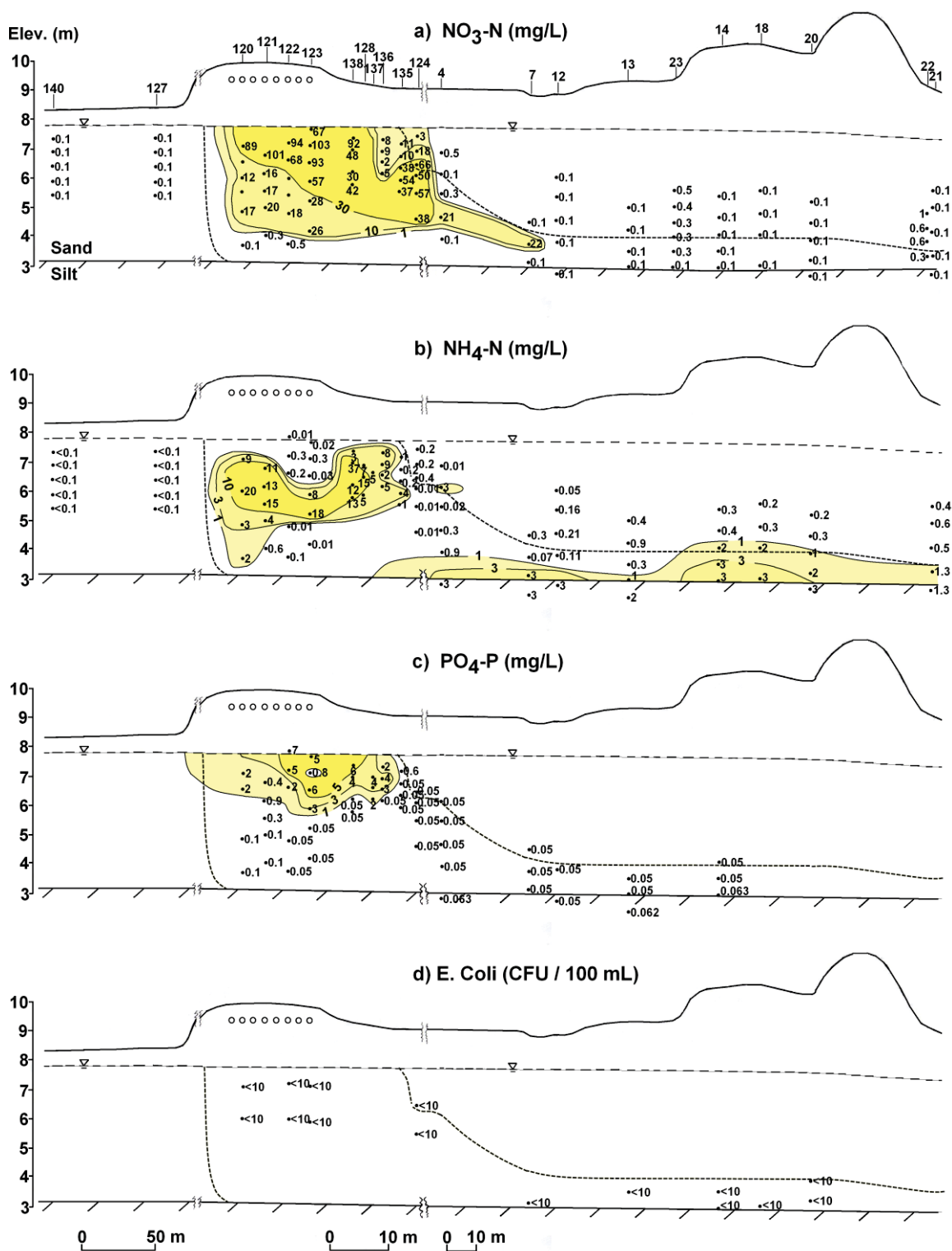


Fig. 5. Distribution of nutrients and pathogens along the plume centreline October, 2010:
a) NO₃⁻-N, b) NH₄⁺-N, c) PO₄³⁻-P and d) E. coli. Dashed line indicates plume core zone
(Na⁺ > 10 mg/L).

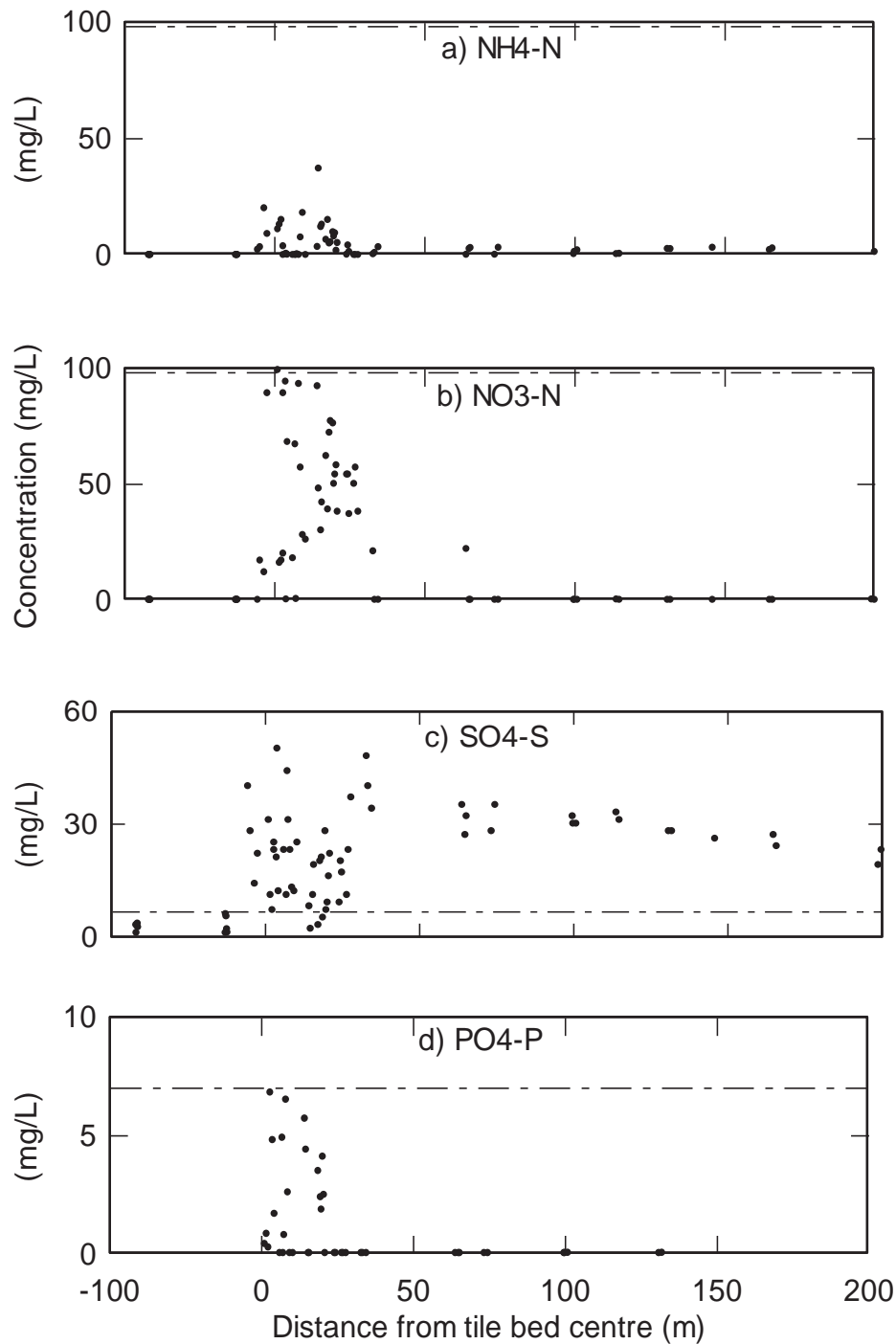


Fig. 6. Concentration profiles of nutrients and $\text{SO}_4^{2-}\text{-S}$ along the plume core and in upgradient wells: a) $\text{NH}_4^+\text{-N}$, b) $\text{NO}_3^-\text{-N}$, c) $\text{SO}_4^{2-}\text{-S}$ and d) $\text{PO}_4^{3-}\text{-P}$. Note that $\text{NH}_4^+\text{-N}$ septic tank mean value from Table 1 (dashed line) is used for both NH_4^+ and NO_3^- panels.

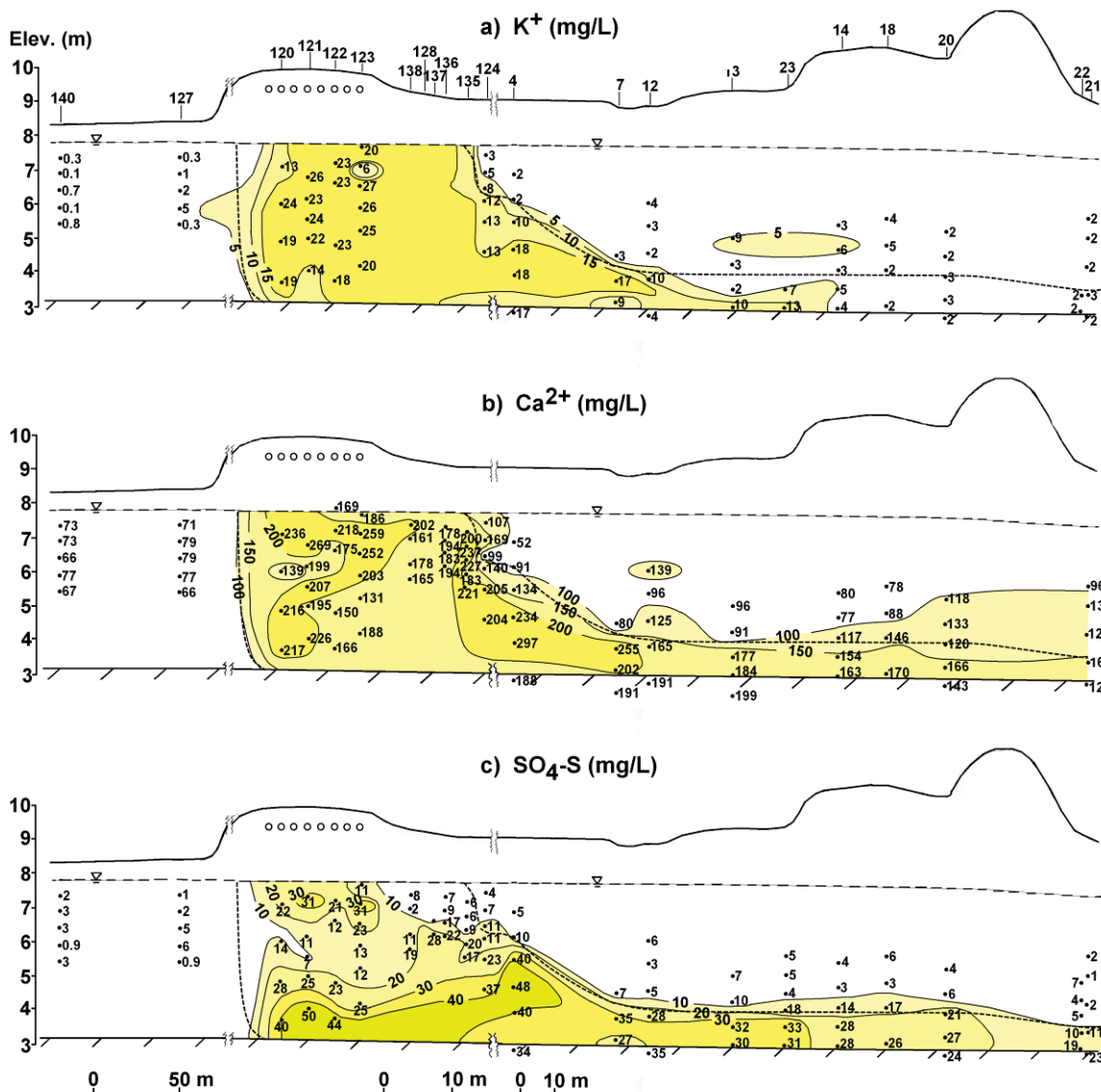


Fig. 7. Distribution of other major ions along the plume centreline, October, 2010: a) K^+ , b) Ca^{2+} , and c) $SO_4^{2-}-S$. Dashed line indicates plume core zone ($Na^+ > 10$ mg/L).

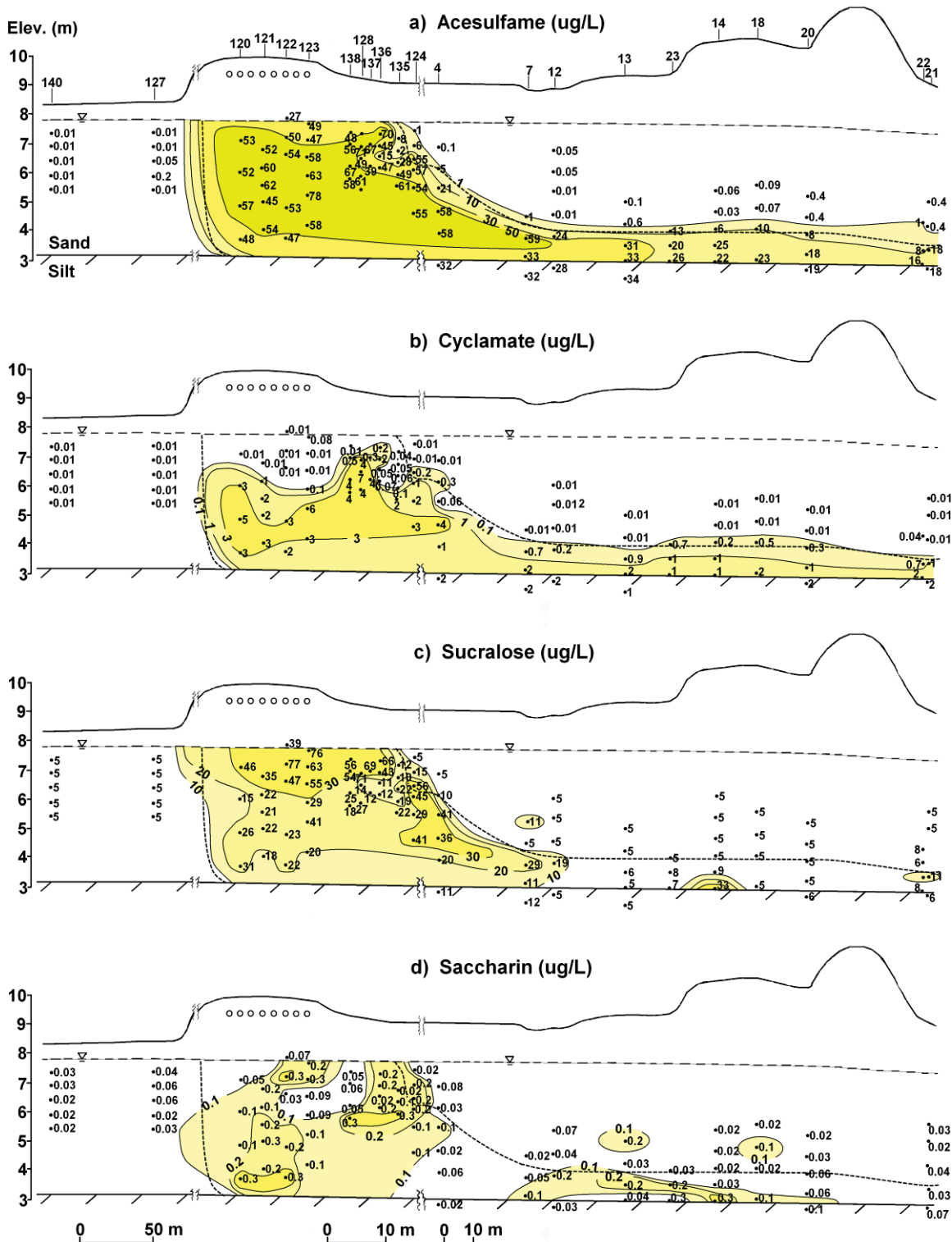


Fig. 8. Distribution of four artificial sweeteners along the plume centre line, October, 2010: a) acesulfame, b) cyclamate, c) sucralose and d) sacharrin. Dashed line indicates plume core zone ($\text{Na}^+ > 10 \text{ mg/L}$).

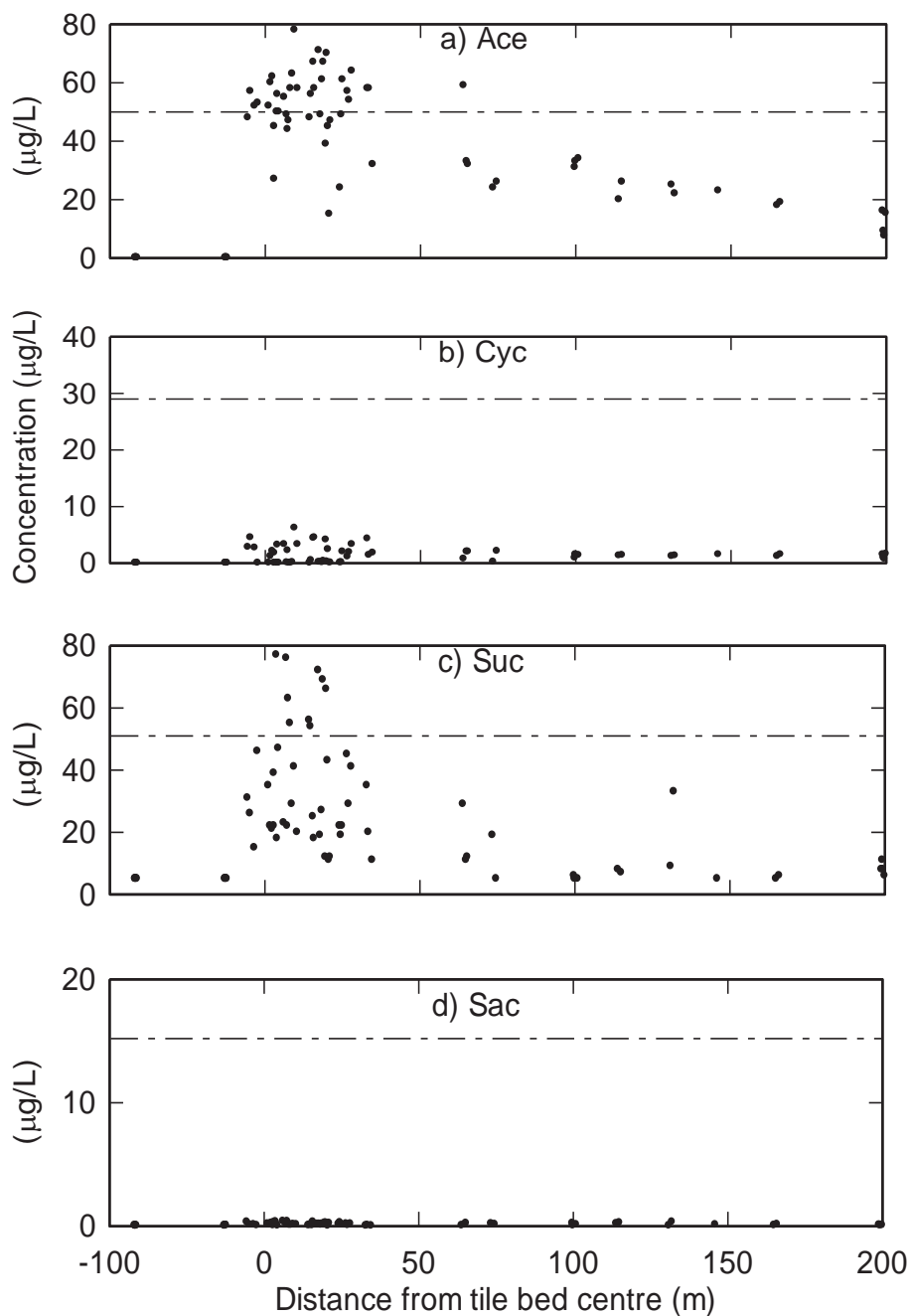


Fig. 9. Concentration profiles of artificial sweeteners along the plume core and in upgradient wells: a) acesulfame, b) cyclamate, c) sucralose and d) saccharin. Dashed lines are mean septic tank values from Table 1.

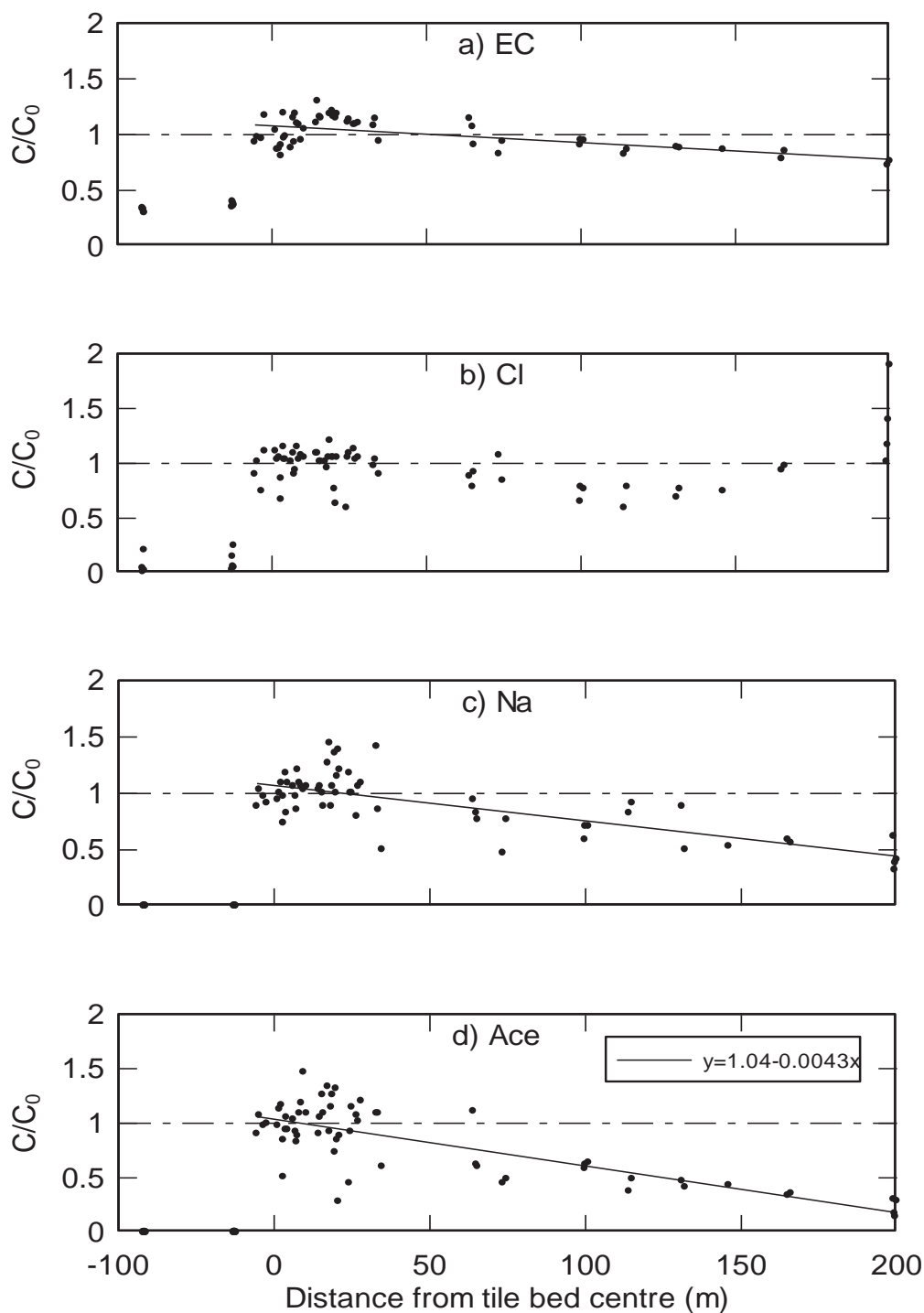


Fig. 10. Normalized concentrations (C/C_0) of indicator parameters along the plume core zone: a) EC, b) Cl^- , c) Na^+ , and d) acesulfame. C_0 values are mean values under the tile bed in bundles 120-123, $n = 20$ (EC, 1244 $\mu\text{S}/\text{cm}$; Cl^- , 52.2 mg/L; Na^+ , 33.9 mg/L; acesulfame, 53.2 $\mu\text{g}/\text{L}$).

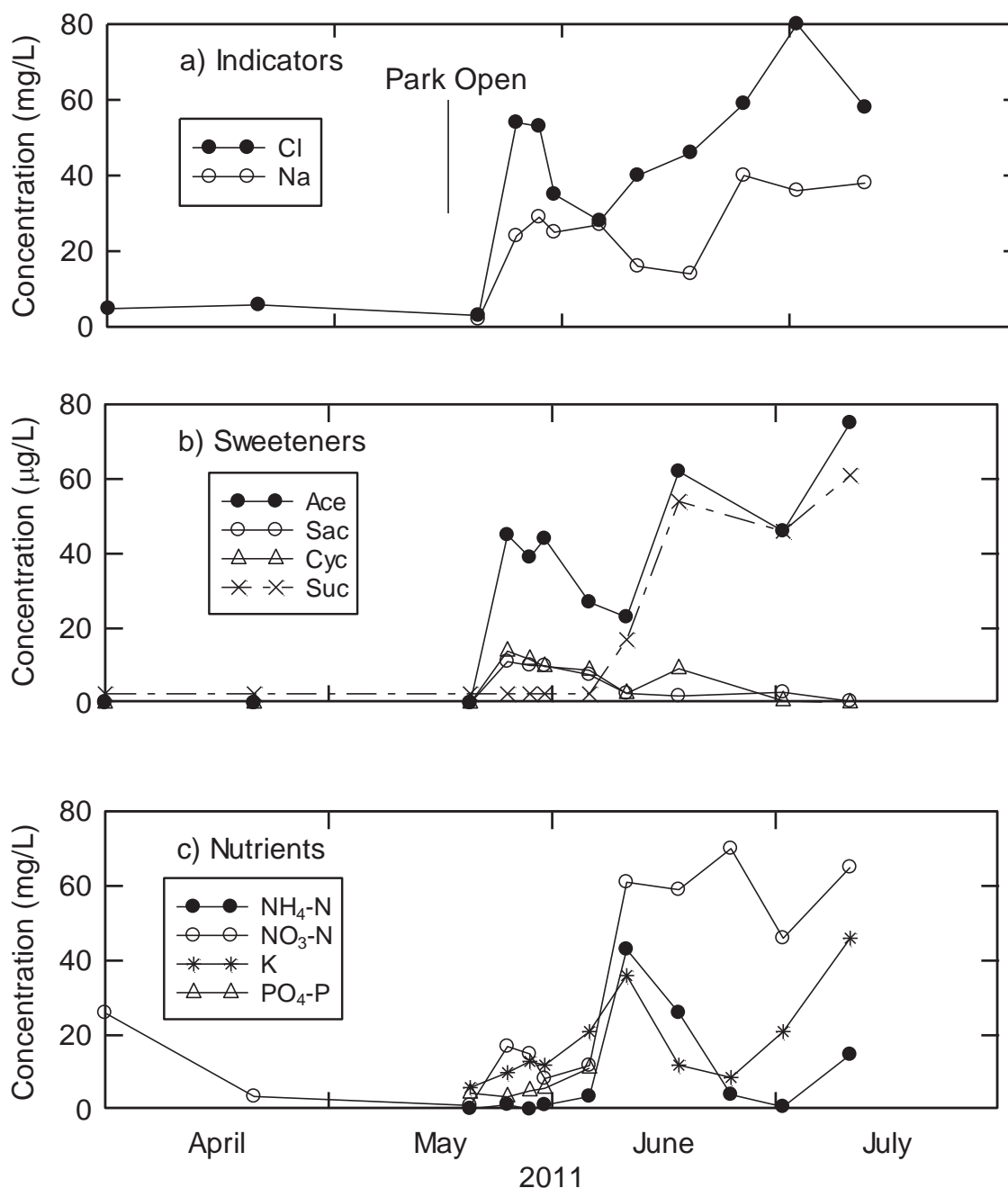


Fig. 11. Breakthrough of wastewater constituents in the shallow water table zone below the tile bed (well 122-2.2 m depth) during campground start-up, spring, 2011: a) indicator parameters, b) artificial sweeteners and c) nutrients. Abrupt increases occurred on May 24, 2011, the day after the first heavy use weekend.

682

Appendix A (Supplemental Material)

Evaluation of tritium/helium-3 ages when degassing has occurred.

684

685 We have followed the approach of Visser et al. (2007), but include terrigenous ^4He and
686 consider the two end member cases of (1) degassing at the water table, and (2) degassing
687 at the time of sampling.

688

689 Case #1 Degassing at the water table with no original excess air.

690

691 The ^3He balance in a sample is:

$$692 \quad {}^3\text{He}_s = {}^3\text{He}_{eq} f_{^3\text{He}} + {}^3\text{He}_s^* + {}^3\text{He}_{terr} \quad (\text{Eq. 1})$$

693 where the subscripts stand for s = sample, eq = equilibrium (sometimes referred to as
694 solubility) terr = terrigenous and

695 $f_{^3\text{He}} = \frac{1}{1 + H_{\text{He}} \Delta V_g}$ is the fraction of ^3He in solution after degassing has occurred, and

$$696 \quad V_g = \frac{1}{\Delta Ne + 1} \Delta 1 \quad \text{is the gas phase volume,}$$

$$697 \quad \Delta Ne = \left(\frac{Ne_s}{Ne_{eq}} - 1 \right) \text{ is the neon deviation from atmospheric solubility,}$$

698 H_{He} is the dimensionless Henrys coefficient for helium, and

699 H_{Ne} is the dimensionless Henrys coefficient for neon.

700

701

702 The superscript * stands for tritogenic (i.e. derived from tritium decay). For each of the
703 subscripted quantities, we define the ratio of ^3He to ^4He (e.g. $R_s = \frac{{}^3\text{He}_s}{{}^4\text{He}_s}$)

704 and substitute these ratios into Eq. 1 to obtain

705

$$706 \quad {}^3\text{He}_s^* = {}^4\text{He}_s R_s - f_{^3\text{He}} {}^4\text{He}_{eq} R_{eq} - {}^4\text{He}_{terr} R_{terr} \quad (\text{Eq. 2})$$

707 The ^4He balance leads to the following expression for terrigenous ^4He

$$708 \quad {}^4\text{He}_{terr} = {}^4\text{He}_s - {}^4\text{He}_{eq} f_{^3\text{He}} \quad (\text{Eq. 3})$$

709 Substituting Eqs. 2 and 3 into the equation of radioactive decay for tritium leads to

$$710 \quad t = \frac{\ln \left(\frac{{}^3\text{He}_s^* + 1}{{}^3\text{He}_s} \right)}{\lambda} \quad (\text{Eq. 4})$$

711

712 Case #2 Degassing at the time of sample collection with no original excess air

713 The ^3He balance is



$${}^3\text{He}_s = ({}^3\text{He}_{eq} + {}^3\text{He}^* + {}^3\text{He}_{terr}) f_{{}^3\text{He}} = f_{{}^3\text{He}} {}^3\text{He}_{eq} + {}^3\text{He}_s^* + {}^3\text{He}_{terr} \quad (\text{Eq. 5})$$

Substituting the ${}^3\text{He}/{}^4\text{He}$ ratios as defined above and solving for ${}^3\text{He}_s^*$ we have

$${}^3\text{He}_s^* = {}^4\text{He}_s R_s - f_{{}^3\text{He}} {}^4\text{He}_{eq} R_{eq} - {}^4\text{He}_{terr} R_{terr} \quad (\text{Eq. 6})$$

The ${}^4\text{He}$ balance leads to the following expression for terrigenic ${}^4\text{He}$

$${}^4\text{He}_{terr} = {}^4\text{He}_s - {}^4\text{He}_{eq} f_{{}^3\text{He}} \quad (\text{Eq. 7})$$

Substituting Eqs. 6 and 7 into the equation of radioactive decay for tritium leads to

$$t = \frac{\ln \left(\frac{{}^3\text{He}_s^*}{{}^3\text{He}_s} + 1 \right)}{\lambda_{{}^3\text{H}}} \quad (\text{Eq. 8})$$